OXIDATION OF SODIUM SULFIDE UNDER AERATION AND ULTRASONIC VIBRATION

ANTARA HUTAMA

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
PERAK, 2010

CERTIFICATION OF APPROVAL

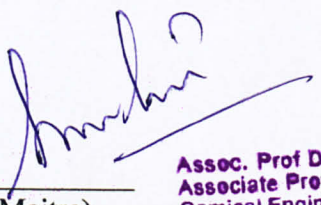
Oxidation of Sodium Sulfide under Aeration and Ultrasonic Vibration

by

Lintang Hutama

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,



(AP Dr. Saikat Maitra)

Assoc. Prof Dr Saikat Maitra
Associate Professor
Cemical Engineering Department
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

LINTANG HUTAMA

Table of Contents

List of Figure and Graph

List of Table

ABSTRACT

This report overviews final year project titled "Oxidation of Sodium Sulfide Using Aeration Technique under Ultrasonic Vibration". This report focus on the Problem statement, Objective, Scope of the Study, Literature Review, Experiment Methodology, Result and Discussion, and Conclusion.

Sodium Sulfide are toxic, corrosive and hazardous. On the plant operation, this Sulphur containing compounds decrease the dissolved oxygen amount in the water. Moreover, the compound has a mortal effect on the bacteria. The objective for this project is to study and analyze the effect of aeration and ultrasonic vibration towards the sodium sulfide oxidation. The scope of study clarifies the project's work boundary to ensure the feasibility of the project within the given time frame. The literature review will focus on the technical side and basic understanding of the project. The Experiment methodology will show the research procedure on doing this project and the proposed Gantt chart. From the result and discussion, it can be seen that this method is feasible to reduce the Sulfide concentration. However, further research need to be done to meet the industrial specification.

CHAPTER 1
INTRODUCTION

1.1. Problem Statement

Sulphur containing compounds is the by-products of industrial processes and wastewater pollutants (*Elvers, et al. 1989; Salazar.1986*). On the other side, the sulphide ions present in the wastewater has a mortal effect on the wastewater treatment bacteria (*Dannenberg, et al. 1992*). The toxic properties of these pollutants decrease the dissolved oxygen amount in the water. Sodium Sulfide is one of the sulfur containing compound which is considered toxic, corrosive and hazardous (*Van den Bosch PLF et. al. 2006*)

1.2 Objective and Scope of the Study

The main objective of this project is to study and analyze the combined effect of aeration and ultrasonic vibration towards the sodium sulfide oxidation. Furthermore, the scope of study for this project is to see the effect of the following parameters towards the final product:

- different aeration flow rate
- different power of ultra sonic vibrator
- different initial sulfide concentration

CHAPTER 2
LITERATURE REVIEW

The literature review will zoom in the title phrased "Oxidation of Sodium Sulfide Using Aeration under Ultrasonic Vibration". It is essential both to the author and to the reader to further understand the concept behind each word. The author will describe in the first sub-section about the characteristic of Sodium Sulfide and why do they need to be further treated.

2.1 Sodium Sulfide

Sada, et. al (1987) has characterized Sodium sulfide as a toxic and malodorous pollutant even at low concentration. The sulfide is generated when microbes decompose organic material containing sulfur in a free oxygen environment. The sulfide exists as waste liquors from paper and pulp mills, anaerobic sewage, and in the oil refineries. When it comes to pollution management, it is necessary to remove sulfide because of its toxicity and unpleasant odor (*pp.1*).

Dannenberg, et. al (1992) further explained the effect of high sulfide content. In the wastewater treatment, the bacteria purified the waste water biologically. The sulfide ions poisoned the bacteria, resulting in the decrement of dissolved oxygen amount in the water *(pp.93)*. The complete oxidation of sulfur containing compounds, before discharging them to the waterways, has been suggested as a possible solution of the environmental pollution problem. *(Chanda, et al. 1984. P.267)*

2.2 Oxidation Process

Ueno et. al. (1978) had defined the possible way of oxidation process happens to the Na2S:

$$2Na_2S + 2O_2 + H_2O \leftrightarrow Na_2S_2O_3 + 2\,NaOH \quad (1)$$

$$2Na_2S + 3O_2 \leftrightarrow 2Na_2SO_3 \quad (2)$$

$$Na_2SO_3 + O2 \leftrightarrow Na_2SO_4 \quad (3)$$

$$Na_2S_2O_3 + 2\,NaOH \leftrightarrow 2Na_2SO_4 + H_2O \quad (4)$$

$$Na_2S + 2O_2 \leftrightarrow Na_2SO_4 \quad (5)$$

As further stated by Ueno, the reaction (3) is far more preferably to occur than reaction (1) and (2). However based on *Holleman AF (2001)* which is quoted from *(Thomson et. al., 2008),* side reaction of:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l) \quad (6)$$

need to be added. In overall, the reaction can be further simplified to be a reaction in series of:

$2Na_2S + 2O_2 + H_2O$	$\leftrightarrow$	$Na_2S_2O_3 + 2\,NaOH$	(1)
$S_2O_3^{2-}(aq) + 2Na^+(aq)$	$\rightarrow$	$S(s) + SO_2(g) + H_2O(l)$	(side reaction)
$2Na_2S + 3O_2$	$\leftrightarrow$	$2Na_2SO_3$	(2)
$Na_2SO_3 + O2$	$\leftrightarrow$	Na_2SO_4	(3)

These chemical reactions are the basic for this project. It is categorized as a reduction oxidation process. The reactions happen in series from 1st reaction to the 2nd reaction, and finally to the 3rd reaction. The reaction can be simplified into:

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

From that reaction, the process can be divided into two:

$8H+ + 8e^- + 2O_2 \rightarrow 4H_2O$ (reduction)

$4H_2O + S^{-2} \rightarrow SO_4^{-2} + 8H^+ + 8e^-$ (oxidation) +

$S^{-2} + 2O_2 \rightarrow SO_4^{-2}$

As seen from the reaction above, the S component undergoes oxidation process where it increases its electron valence from S^{-2} to S^{+6}. In the other side, the O component undergoes reduction process from O^0 to O^{-2}.

2.3 Various Oxidation Methods Done

The wet air oxidation process has been applied to the treatment of a wide variety of wastewater *(Dietrich, 1985)*. It is further described by *Copa, et al (1992)* that the wet air oxidation has been applied to the treatment of spent caustic liquor generated in the petrochemical and refinery industry. This spent caustic contains sulfides, mercaptans, and phenol as well as emulsified hydrocarbons. Wet air oxidation refers to a process which involves an aqueous phase oxidation of organic and inorganic material at elevated pressure and temperature. In wet air oxidation, oxidation and hydrolysis occur at temperatures in the range of 150 to 320 °C and at corresponding pressure ranging from 20.4 to 204 atm. Oxygen, from compressed air or pressurized oxygen gas serves as the oxidizing agent. This process has provides an effective means of disposing spent caustic liquor from the petrochemical and refinery industry (please refer to Appendix 1 The Wet Air Oxidation of Sulfide at a temperature 100 °C and Appendix 2 Percent Conversion of Reduced Sulfur to Sulfate in Wet Air Oxidation).

On the other side, alternative pilot scale project has been investigated to oxidize sodium sulfide. *Sada, et. al (1987)* used activated carbon to oxidize sodium sulfide. The rate of sulfide oxidation in aqueous slurries of activated carbon particles at pH 8-12 were investigated by using a stirred vessel with a gas sparger. The oxidation rate at pHs 10 and 12 was apparently expressed as about half order with respect to the dissolved oxygen concentration and first order with respect to the concentration of sulfide in the liquid phase.

Mallik and Chaudhuri (1998) used air oxidation method with the presence of coal fly ash. The coal fly ash is a potential heterogeneous catalyst in the oxidation of aqueous Sodium Sulfide at 30 °C. Mineral phases of fly ash are more active than that of unburned carbon present in it. From the author's perspective, *Mallik and Chaudhuri* had found an alternative solution for the small scale industry that needs a cheap catalyst to treat their waste. Eventually, activated carbon was proposed as a potential catalyst for the air oxidation by some researchers. Unfortunately, the price and separation cost of the activated carbon is expensive as compared to the Coal Fly Ash. *Mallik and Chaudhuri* found out that Coal Fly Ash is easy to be separated by gravity from the treated effluent. The coal fly ash is economically and technically viable for small scale unit.

Linkous, et. al (2004) used photochemical oxidation to produce Hydrogen and Sulfur from Aqueous Sodium Sulfide. The sulfide ions, principally bisulfide, could be photochemically oxidized under UV light to produce sulfur, complexed mainly as disulfide ion, while water was reduced to produce hydrogen in a complementary redox process. This was accomplished without catalyst to be deactivated or electrodes susceptible to passivation and corrosion. The quantum yields of the H2 evolution reaction using a low-pressure mercury lamp were as high as 27% higher than other photolytic systems, By matching the UV light input to flow rate in a circulating system, the quantum efficiencies could likely be further increased. *Couvert, et. al. (2006)* treated the odorous sulphur compound by chemical scrubbing with hydrogen peroxide. The use of hydrogen peroxide instead of chlorine is a superior way to explore. It doesn't generate any harmful by products. Moreover, its consumption per mole of sulphur compound is quite acceptable. Indeed, the reaction stoichiometry is almost respected because its decomposition has been reduced by the addition of poly-α-hydroxyacrylic acid in the scrubbing solution.

2.4 Aeration

2.4.1. Aeration Fundamental

Based on *Mueller et al. (2000):* Aeration is the transfer of oxygen to the biologically active masses of organisms within these systems. Transfer of oxygen occurs between two phases. Oxygen molecules are initially transferred from gas phase to the surface of the liquid. Equilibrium is quickly established at the gas-liquid interface.

2.4.2. Factors affecting the rate of O_2 oxidation of sulfide solution

In this section, the author had cited the work from *Kuhn (1983).* In his opinion, the factors that affect oxidation are:

- Induction Period

The onset of the oxidation is preceded by an induction period. In some cases (*Selmeczi, 1966; O'Brien and Birkner, 1977*) this was not seen. *Chen and Morris (1972)* related the length of the induction time inversely to the initial rate constant. *Snavely and Blount (1969)*, who present their data in term of log(time), showed the effect again without comment. *Cline and Richard (1969)* referred to the apparent slow rate at the beginning of the reaction which was significant in some studies

- Temperature

Selmeczi (1966) followed oxidation of 10 parts/106 H2S solutions (pH 6-8) at 10, 25, and 38 °C and reported an outstanding temperature effect. The concentration of dissolved oxygen decrease with increasing temperature. *Cooper (1974)* has studied oxidation of "black liquor" (a sulphide rich effluent) and found the oxidation rate increase from 0.234 gr/dm^3.s Na_2S at 102 °C to .983 gr/ dm^3.s at 110 °C. Cooper also states in the other paper that the threefold rate increase from 60 to 82 °C followed by a leveling off possibly due to oxygen loss. *Bowers (1966)* showed an Arrhenius plot over much the same range of temperature, though it was rectilinear, which may be due to the presence of the added catalyst.

- pH

Chen and Morris reported a complex relationship between pH and the rate of oxidation. The rate increased from pH 6, reaching a maximum at pH 8.5, declining to a minimum at 9.3 and attained a second maximum (approximately the same rate as the first) at pH 11.5. Cooper reported an exponential increase in rate over the range pH 10.5 to 13. Snavely and Blount (200 parts/106 H2S, 25 oC) showed little difference in oxidation rate between pH 2.2 and 6.5, but a very substantial increase at pH 11.5

Alferova and Titova reported the effect of pH on the various oxidation steps starting from S(-II). In general, they found that extremes of pH led to higher rates, though some sulphides (e.g iron sulfide) were nire susceptible to acid catalysis, and others (e.g Cu_2S) more to alkaline catalysis. It was stated that the work was carried out with and without addition of activated carbon, but the results do not make clear when this addition was present.

- Sulphide ion concentration

Chen and Morris showed a series of linear plots between log ($\sum S^{-2}$) and log rate of oxidation at pH 6.9, 7.2, 8.34, 9.36, 10.3, all of which had the same gradient at 25oC. O'Brien et al. found a reaction order of 0.56 at 49 °C as did Chen and Morris though they worked at 25 oC

- Effect of O_2 concentration

Chen and Morris found a linear log-log relationship between O2 partial pressure and rate of oxidation over the range 1.6 to 8 x 10-4 M (O2). O'Brien cited a first order dependence on O2 partial pressure as did Leschinskaite et al. Lefers et al. found a reaction order of 0.56 at 49 °C as did Chen and Morris though they worked at 25 oC

- Effect of Neutral Salt

According to Alferova et al. neutral salts somewhat accelerated the oxidation reaction at contstant pH, which they explained simply in terms of an ionic strength effect, without further comment.

- Bacterial action and the effect of organic species

Bacterial action can be important in the oxidation sequence and bacteria can reduce sulphates or oxidize sulphur to sulphite/ sulphate. Sorokin suggested, quoting earlier work of Wheatland, that air oxidation of sulphide leads to thiosulphate formation, with bacterial action responsible for further oxidation to sulphate. Cline and Richards quoted several references to suggest that organic species inhibit air oxidation of SO3-2 though Chen and Morris suggested that (S-II) is an inhibitor for this final stage

2.5 Ultrasonic and its usage

Lempriere (2002, pp.1) described: Ultrasonic is the science and exploitation of elastic waves in solids, liquids, and gases, which have frequencies above 20 khz (the nominal limit of human hearing).

Although ultrasonic technology is famouos for its use in the Medical Service industry, the usage of ultrasonic is widely varied in the Chemical Discipline. Ultrasound applied during chemical or electrolytic etching often increases the rate of material removal by a factor *(Ensminger, 1988, pp.495)*. On treating juices and wine, Ultrasonic applied to newly ferment alcoholic beverages produces effects similar to those resulting from a long period of aging *(Bachman, 1937)*. On the treatment of sewage, ultrasonic is used to clean or strip masses of material from the upstream side of a filter and to concentrate the material in an area from which it can be easily removed *(Davidson, 1970)*.

On the extraction process, *Ensmenger (1988, pp. 497)* had put together different project into his book. *Adamski and Socha (1967)* showed that ultrasound had about the same effect as heat in removing capsaicine from the fruit *Capsicum annum* and did not cause any decomposition of capsaicine. *Chen and Fairbanks (1968)* have shown that ultrasonic energy at 20 kHz can increase the rate of flow of oil through sandstone. *Chen and Chon (1967)* found that increased extraction efficiency results from applying ultrasonic at intensities above the cavitation threshold during continuous liquid-liquid extraction processes. They attributed the increased effectiveness to increase turbulence which may also increase the interfacial area of contact between the phases, thus enhancing mass transfer.

On the field of Chemical Synthesis, it was seen that chemical activity, especially oxidation reaction, may be accelerated, sometimes manifold, under the influence of ultrasonically produced cavitation *(Ensminger, 1988, pp.391). Anon (1953)* found out that ultrasound can be used to activate transition metal complexes so that they will catalyze organic reactions. *Enseminger (1988, 504)* further state that the stoichiometry and the catalytic chemistry initiated by ultrasound differ from those of either thermally or photolytically induced reaction of the same system.

In catalytic reactions, Enseminger wrote out *Boudjouk's (1984)* discovery that ultrasound cleans surfaces of heterogeneous metal catalyst, removing impurities such as metal oxides and bringing the reactant materials into more intimate contact with the catalyst surfaces. The result is increased reaction rates. *Boudjouk* also claims that the ultrasonic cleaning action inhibits side reactions by washing the product away from the catalyst before they can undergo further reaction

Mason (1986) reviews the effect of ultrasonic energy on chemical reactions, including many which don't occur without ultrasonic stimulation. Based on Enseminger perception, *Mason* claims that ultrasonic cleaning action on the surface of metallic catalyst is helpful but it is not sufficient to explain the extent of the sonochemically enhanced reactivity. Interfacial contact area is an important parameter in the ultrasonic acceleration of chemical activity whether between reacting constituents or between the reacting materials and catalysts. Powder type constituent are dispersed ultrasonically in the media and thus increase available contact surface. This contact surface is further increased by partially size reduction by fracture in an ultrasonic field.

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

Two methodologies are able to be done related with this experiment. The differences between the methodologies appear because each methodology is using different Sulfide Measuring Tools. Methodology A is using Hach UV Spectrometer DR 5000 in room 05-00-01. Methodology B is using the Shimadzu UV Spectrophotometer in room 04-02-09. The difference in Sulphide Measuring Tools has led to different kind of reactant preparation. For this project, Methodology A is selected since the Spectrophotometer is located in the same place as the preparation site. However, the details on General Preparation for both Methodology A and Methodology B is discussed in this section.

Figure 3-1. Hach UV Spectrometer

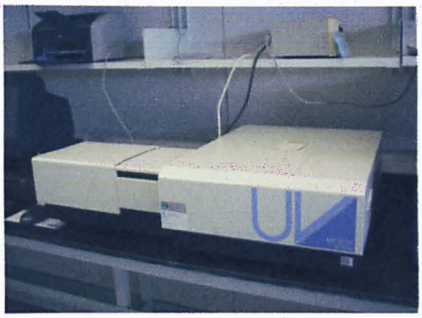


Figure 3-2. Shimadzu UV Spectrophotometer

3.1.1 General Preparation

Step 1. Preparing the Na2S

a) The Na2S used in this project is the synthesis Na2S

Figure 3-3. Sodium Sulfide Hydrate

b) The Na2S comes in the solid form with 60% purity
c) Based on the experiment, when 1 gr of Na2S is diluted in 1liter of distilled water, the solution gives 600 ppm Na2S concentration
d) Prepare the desired Na2S concentration
e) Once the Na2S is ready, put it inside a 1L bicker

Step 2. Preparing the Aerator

a) Open the Air Line
b) Connect the host to the Air Diffuser
c) Set the Flow Rate of the air to the desired amount

Step 3. Preparing the Ultrasonic vibrator

a) Fill the ultrasonic vibrator with 8 L distilled water
b) Turn on the Ultrasonic Vibrator
c) Set the value of Ultrasonic Power and Heating value
d) Set the Time Duration

Note

a) For normal experiment, the Ultrasonic Power is set at 100 W
b) The Ultrasonic duration is set at 60 minutes
c) For normal experiment, the heating value is not used

Step 4. Na2S oxidation under Aeration and Ultrasonic Vibration

a) Take the beaker and put it inside the ultrasonic vibrator which is filled with 8 L distilled water
b) Put the Air diffuser inside the bicker
c) Turn on the Ultrasonic Vibrators
d) Wait until the duration of the time is reached

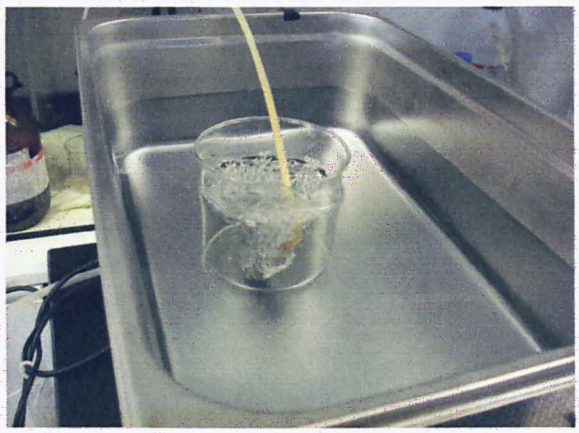


Figure 3-4. Overall look of the experiment

e) Collect10 mL of sample. Put the sample in the bicker
f) Take the following reading from the Sulphide : Dissolved Oxygen, and temperature

Figure 3-5. DO meter and thermometer

g) Collect 10mL of sample Sulphide from the bicker
h) Use a pippet to get the sample
i) The amount of sample needed depends on the methodology that is being followed

3.1.2 Methodology A

a) Collect 2 mL of oxidized Na2S sample
b) Put 2 mL of Carbon Disulfide so that it will absorb the fundamental sulphur left over in the sample
c) Put the samples in vertical position
d) Wait 10 minutes so that the carbon disulfide- sulfur settles down
e) Dilute the sample 5 times with distilled water. The sample is now 10 mL
f) Get 10 mL of Distilled Water
g) Put 0.5 mL of Reagent I and Reagent II into both the sample and the distilled water
h) Shake both the sample and the distilled water well
i) Wait for 5 minutes

Figure 3-6. Carbon Disulfide

j) Put the distilled water in the Hach UV Spectrophotometer
k) Set the distilled water as a zero Sulphide condition
l) Let the distilled water inside the Hach UV Spectrophotometer
m) Put the sample inside the Hach UV Spectrophotometer
n) Record the sulphide content from the sample
o) Multiply the result with 0.3 to get Sulphide content in part per million (ppm)
p) The actual concentration of Sulphide left is generated

Figure 3-7. Inside look of the Hach Spectrophotometer

3.1.3 Methodology B

a) Collect 1 mL of oxidized Na2S from the bicker
b) Put 2 droplets of carbon disulfide so that it will absorb the fundamental sulphur left over in the sample
c) Put the sample in a vertical position.
d) Wait 10 minutes so that the carbon disulfide- sulfur settles down
e) Dilute the sample with 99 mL of distilled water. The sample is now 100 mL

Shimadzu Spectrophotometer Concept

Shimadzu spectrophotometer basic idea is to get the concentration of a sample based on the standard curve that we have key in before. The basic concept of this spectrophotometer is to provide a concentration measurement based on the ultraviolet wavelength .To be noted here, every different concentration have different absorbing ability. So the standard curve is a plot between concentrations versus absorption capacity.

Currently our sample also has specific range of absorption. And we don't know what the exact concentration is. So in here, the spectrophotometer will detect the absorbing capacity of our sample. Next, it will compare the current sample's absorbing capacity with the standard curve that we have plotted before. Below are the steps to conduct the Shimadzu Spectrophotometer start up

Spectrophotometer Start Up

a) Turn on Shimadzu spectrophotometer
b) Turn on the computer connected to Shimadzu UV spectrophotometer
c) Enter the UV Probe Software
d) Click Connect
e) A Dialog Box will appear on the computer screen
f) Wait until all box becoming green, Click ok

Sulphide measurement method

a) Open the respective Standard Curve
b) Get two empty sample cells
c) Notice that it is very important to have the sample cell clean especially at the side part of the cell
d) Put the empty sample cells inside the Spectrophotometer
e) Close the cover of the Spectrophotometer
f) Click baseline in the UV Probe Software
g) Key in the value from 300 to 200 nm. Click ok
h) Take the sample cells out. Fill both of them with distilled water
i) Put the sample cells inside the Spectrophotometer. Close the cover of the Spectrophotometer
j) On the monitor, give name to the sample that will be detected
k) Click on the concentration column. Click auto zero in the Probe Software
l) The value in concentration column is now filled with the concentration
m) Multiply the given concentration with 100
n) Now the actual sulphide concentration is attained

3.2 Overal Research Methodology

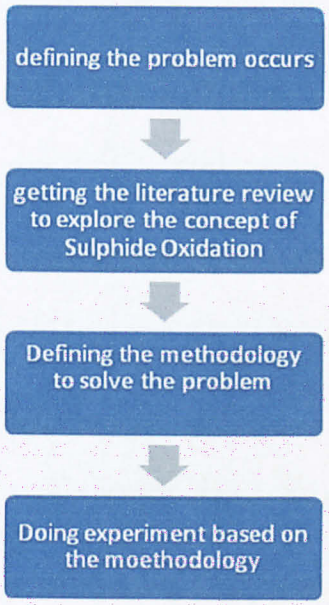


Figure 3-9. Overall Research Methodology

3.3 Project Activities

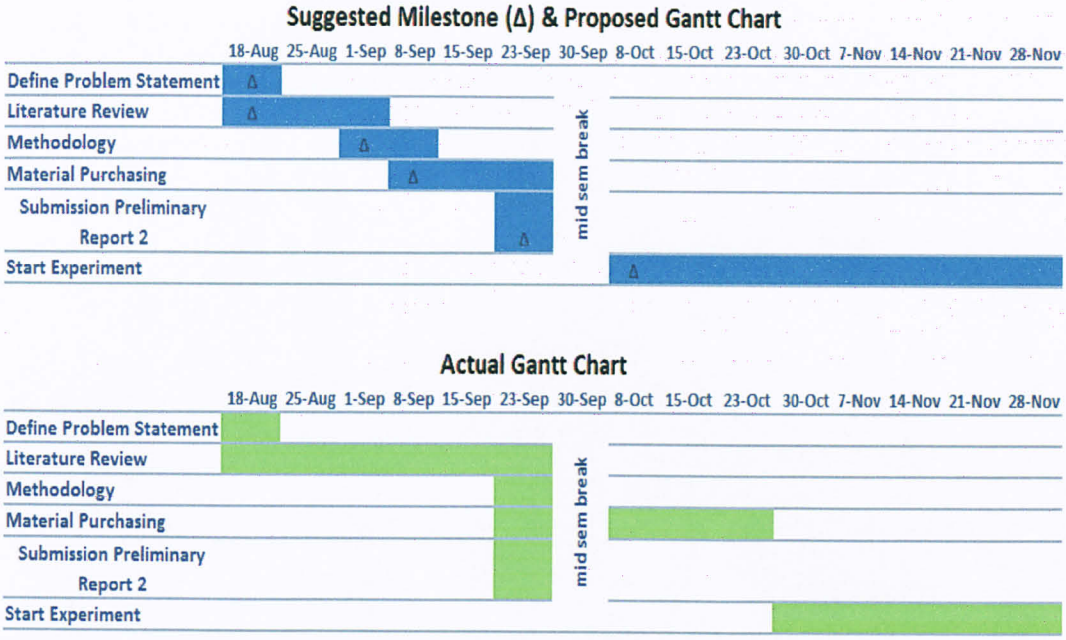


Figure 3-10. Suggested Milestone, Proposed Gantt Chart, and the Actual Gantt Chart

3.4 Tools and Equipment Used

3.4.1 Chemicals Used

- Sodium Sulfide Hydrate 60%
- Acetone
- Distilled Water

3.4.2 Tools Used

- Bicker
- Pipette
- Ultrasonic Vibrator
- Air Diffuser
- Shimadzu UV-Vis Spectrophotometer
- Sample Cell

- pH meter
- Dissolved Oxygen meter
- Stop Watch
- Software UV Probe

3.5 Variables

3.5.1 Manipulated Variable:

- F= Air Flow Rate (4 L/min, 6 L/min, 8 L/min)
- P= Ultrasonic Power (100%, 60%, 20%)
- M= Na2S initial concentration (1000 ppm, 800 ppm, 600 ppm)

Controlled Variable (variable to be determined after oxidation takes place)

- Sulphide concentration left (ppm)
- Dissolved Oxygen (mg/L)
- Sample temperature (^{o}C)

CHAPTER 4
RESULT AND DISCUSSION

This chapter is divided into several parts. In section 4.1, we will show that the addition of CS2 affect the Spectrophotometer Reading. This is to further justify our methodology in the addition of CS2. In section 4.2, we will manipulate the Initial Sulphide Concentration and see how different Initial Sulphide Concentration effects the final Sulphide Concentration. In section 4.3, we manipulate the Ultrasonic Power and see how different in Ultrasonic Power effects the final Sulphide Concentration. In section 4.4, we manipulate the Air Flow Rate and see how different Air Flow Rate effect the final Sulphide concentration.

4.1 Result with CS2 drop and with no CS2 drop

As been stated by *Holleman AF (2001)* which is quoted from *(Thomson et. al., 2008),* side reaction of:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l) \quad (6)$$

is unavoidable. The side product of solid Sulphur affects the reading of remaining sulphide. Solid sulphur submerged inside the sample tube, blocking the UV spectrum from getting the total Sulphide inside the sample. CS2 is added to absorb the solid sulphur inside the sample. The UV spectrum is now able to detect the right amount of Sulfide content.

1000 ppm, 4 L/min air, 100% Ultrasonic Power

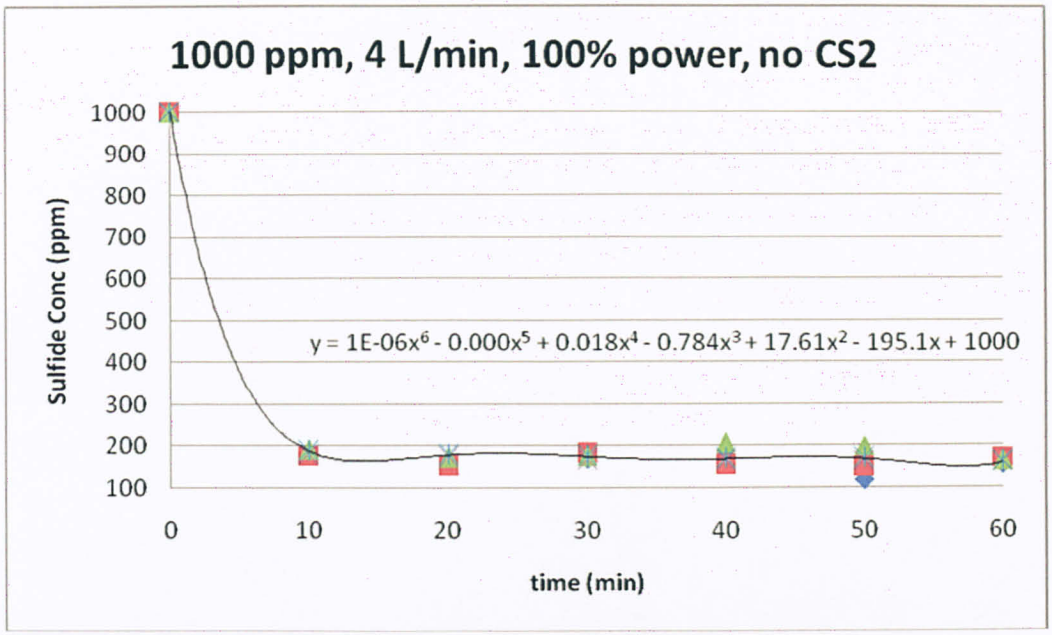
time	1st	2nd	3rd	4th	5th	Average
0	999.999	999.999	999.999	999.999	999.999	1000
10	179.7	179.4	192	180	189	184.02
20	157.2	152.4	173.7	173.7	180	167.4
30	170.4	182.7	176.7	168	176.7	174.9
40	177	156.6	207.6	165	171	175.44
50	119.4	149.7	201	166.8	170.7	161.52
60	157.2	172.2	165	162	162	163.68

Table 4.1-1. Change of Sulfide Concentration with no CS2

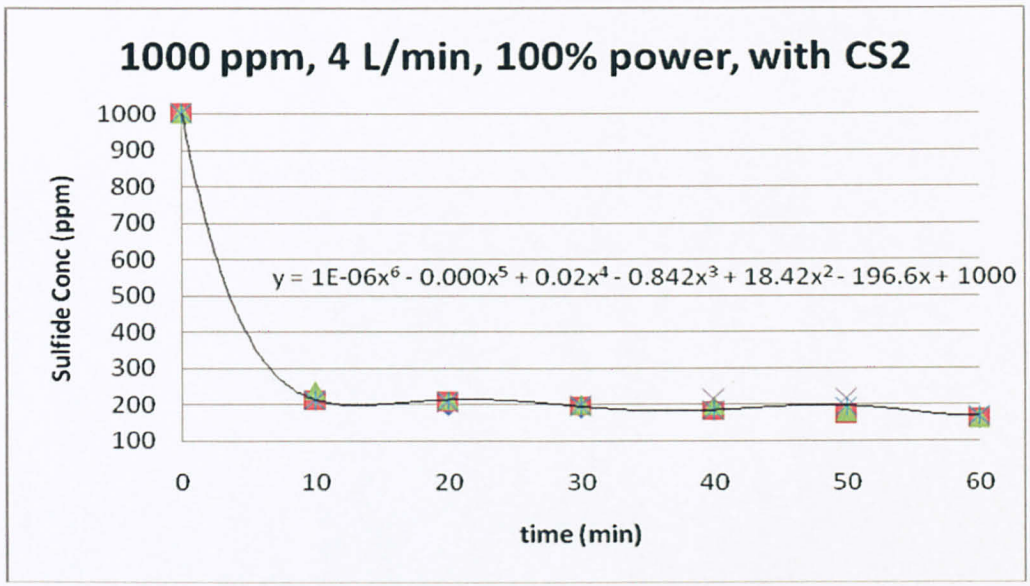
1000 ppm, 4 L/min air, 100% Ultrasonic Power

time	1st	2nd	3rd	4th	5th	average
0	999.999	999.999	999.999	999.999	999.999	999.999
10	209.7	210.3	240	212.1	210.9	216.6
20	195	206.7	211.2	203.7	211.2	205.56
30	188.964	198.3	200.4	201.3	192.3	196.2528
40	182.67	182.934	198.3	213	182.7	191.9208
50	172.965	170.631	177.9	219.3	194.7	187.0992
60	159.4974	163.164	160.698	166.5	169.5	163.8719

Table 4.1-2. Change of Sulfide Concentration with CS2



Graph 4.1-1 Trend without CS2



Graph 4.1-2 Trend with CS2

As we can see from the results, the sulfide concentration left shows a higher number when we add CS_2. The CS2 is proven to attract the elemental Sulphur down. The sample is now clean and ready for the Spectrophotometer reading. Therefore, the correct amount of sulphide concentration left is approaching the actual value. From now on, CS2 would be added to the entire sample.

4.2 Result for Different Initial Sulphide Concentration

time	1st	2nd	3rd	4th	5th	average
0	1000	1000	1000	1000	1000	1000
10	209.7	210.3	240	212.1	210.9	216.6
20	195	206.7	211.2	203.7	211.2	205.56
30	188.964	198.3	200.4	201.3	192.3	196.253
40	182.67	182.934	198.3	213	182.7	191.921
50	172.965	170.631	177.9	219.3	194.7	187.099
60	159.497	163.164	160.698	166.5	169.5	163.872

Table 4.2-1 1000 ppm, 4 L/min air, 100% Ultrasonic Power, With CS_2

time	1st	2nd	3rd	4th	5th	6th	average
0	800	800	800	800	800	800	800
10	159	141.6	154.5	150.9	140.1	149.7	149.3
20	129.6	131.4	148.5	134.4	137.4	147.3	138.1
30	135.6	139.5	143.7	140.1	138.9	146.1	140.65
40	144.6	154.5	134.1	137.4	148.2	166.5	147.55
50	121.8	132.6	120.6	137.1	148.8	147	134.65
60	123.6	120.9	139.5	144.3	172.5	169.8	145.1

Table 4.2-2. 800 ppm, 4 L/min air, 100% Ultrasonic Power, With CS_2

time	1st	2nd	3rd	4th	5th	average
0	600	600	600	600	600	600
10	111.6	108	107.4	109.5	110.1	109.32
20	117.3	102	99.9	105	108	106.44
30	103.8	99	102.9	103.2	100.5	101.88
40	111.9	93	99.3	100.5	104.4	101.82
50	96.3	99.6	93.3	95.7	97.5	96.48
60	104.7	96.6	96.6	94.5	93.6	97.2

Table 4.2-3. 600 ppm, 4 L/min air, 100% Ultrasonic Power, With CS_2

initial 1000 ppm			initial 800 ppm			initial 600 ppm		
time	DO (mg/L)	T (oC)	time	DO (mg/L)	T(oC)	time	DO (mg/L)	T (oC)
0	8.67	20	0	8.67	20	0	8.67	20
10	8.11	23.6	10	8.5	23.6	10	8.6	21.3
20	8.39	24.2	20	8.45	24.2	20	8.5	23.6
30	8.38	24	30	8.69	24	30	8.45	24.2
40	8.19	25.5	40	7.92	25.5	40	0.69	24
50	8.51	25.8	50	7.91	25.8	50	7.92	25.5
60	8.43	27.4	60	7.49	27.4	60	7.91	25.8

Table 4.2-4. DO and Temperature Change for respective Initial Na_2S

From table 4.2-1, table 4.2-2, and table 4.2-3, we can see different remaining sulphide concentration after 60 minutes. We can conclude in the table below

initial (ppm)	1000	800	600
remaining average after 60 minutes (in ppm)	163	145.1	97.2
drop (ppm)	837	654.9	502.8

Table 4.2-5 The Sulfide Drop for Different Initial Sulfide Concentration

From table 4.2-2 and table 4.2-3 interesting trend can be seen in the 60th minutes. We can see that the sulphide content increased. In table 4.2-2, the sulphide content increased from 134.65 ppm to 145.1 ppm. In table 4.2-3, the sulphide content increased only from 96.48 to 97.2 ppm. What is suspected from this increment trend is the nature of reversible reaction as stated by Ueno et. al. in 1979. As stated in the literature review, Ueno et al stated that five reaction occurs during the oxidation of Sodium Sulfide. The oxidation process proceeds from Na_2S to $Na_2S_2O_3$, Na_2SO_3, or Na_2SO_4. The following equations express the reaction:

$$2Na_2S + 2O_2 + H_2O \leftrightarrow Na_2S_2O_3 + 2\,NaOH \quad (1)$$

$$2Na_2S + 3O_2 \leftrightarrow 2Na_2SO_3 \quad (2)$$

$Na_2SO_3 + O2 \leftrightarrow Na_2SO_4$ (3)

$Na_2S_2O_3 + 2\ NaOH \leftrightarrow 2Na_2SO_4 + H_2O$ (4)

As further stated by Ueno, the reaction (3) is far more preferably to occur than reaction (1) and (2). Based on reaction (3) stated by Ueno, subjective reasoning was taken. As the amount of Na_2S is reduced by time, the amount of Na_2SO_4 is increasing with time. As the amount of Na_2SO_4 increased, reaction (3),(4),(5) becomes reversible. Therefore, the change of reaction direction (3), (4), (5) will affect reaction (1),(2). We can see the reaction's direction to be:

$Na_2SO_4 \leftrightarrow Na_2SO_3 + O2$ (3)

$2Na_2SO_4 + H_2O \leftrightarrow Na_2S_2O_3 + 2\ NaOH$ (4)

$Na_2S_2O_3 + 2\ NaOH \leftrightarrow 2Na_2S + 2O_2 + H_2O$ (1)

$2Na_2SO_3 \leftrightarrow 2Na_2S + 3O_2$ (2)

When the reversed reaction happens, the amount of Na_2S will increased. It is the biggest possibility when the sample was taken. This is how the amount of Na_2S will increase when the sample was taken.

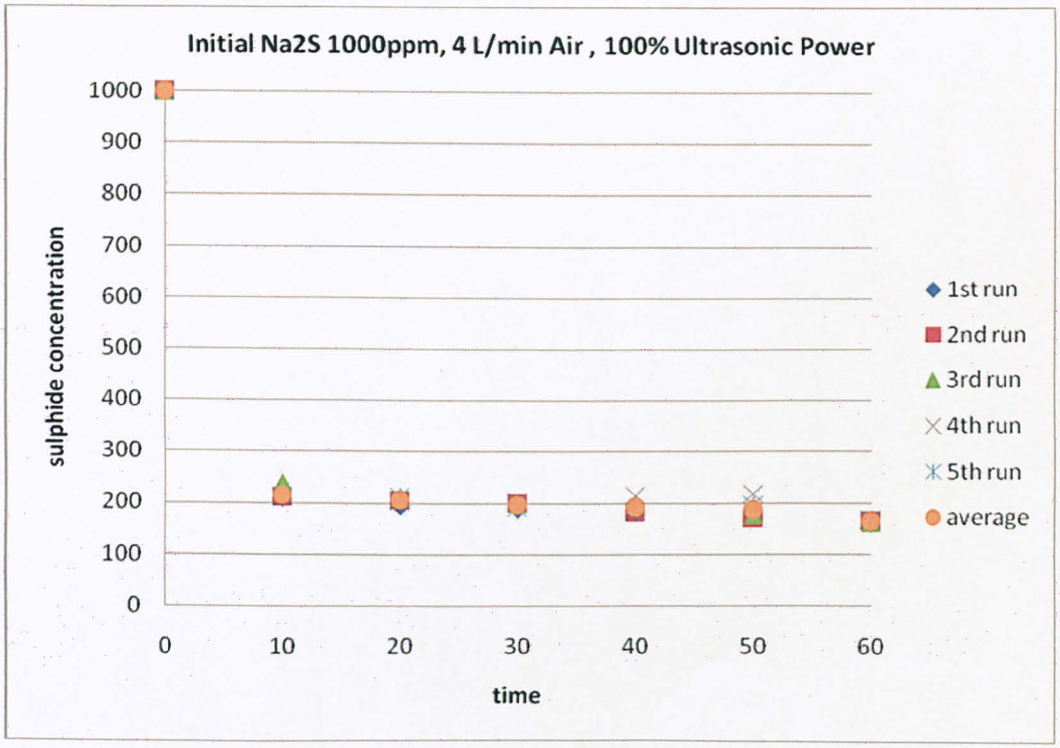
Another interesting result that we can discuss is the relation between amount of Dissolved Oxygen and Temperature increase. As *Selmeczi(1966)* done the oxidation of 10 parts/106 H2S solutions (pH 6-8) at 10, 25, and 38 °C, he managed to find out an outstanding temperature effect. The concentration of dissolved oxygen decrease with increasing temperature. The same result can also be seen here. As the temperature of the Na_2S increase, the amount of dissolved oxygen increased. This is a good indication for the occurrence of oxidation. the fact was supported by *Cooper (1974)* who has studied oxidation of "black liquor" (a sulphide rich effluent) and found the oxidation rate increase from 0.234 gr/dm^3.s Na_2S at 102 °C to .983 gr/ dm^3.s at 110 °C. Cooper also states in the other paper that the threefold rate increase from 60 to 82 °C followed by a leveling off possibly due to oxygen loss.

Let us now compare the sulphide drops from Initial Na_2S of 600 ppm with the wet air oxidation proposed by *(Dietrich, 1985)*. Dietrich applied the Oxidation under High Pressure at 100 °C.

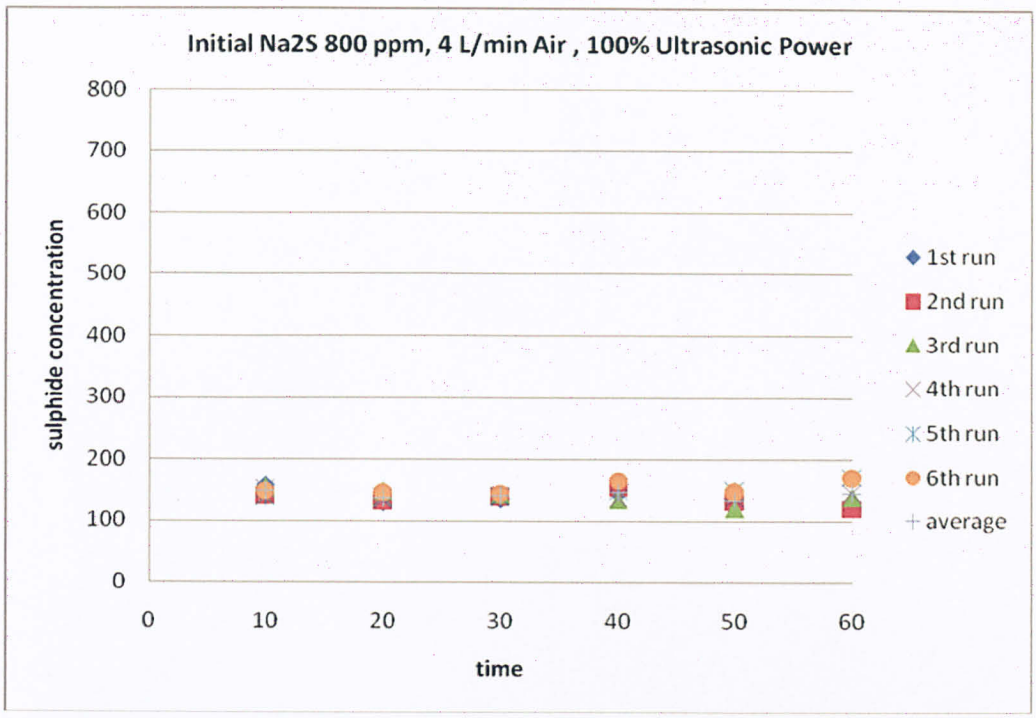
Wet Air Oxidation		Ultrasonic And Aeration
Time At Temperature, Min	Sulfide As S (ppm)	Sulfide (ppm)
Influent	378	600
15	128.4	106.4
30	3.6	101.88
45	0	96.48
60	0	97.2

Table 4.2-6 Comparison between Dietrich Wet Air Oxidation with the Current Project

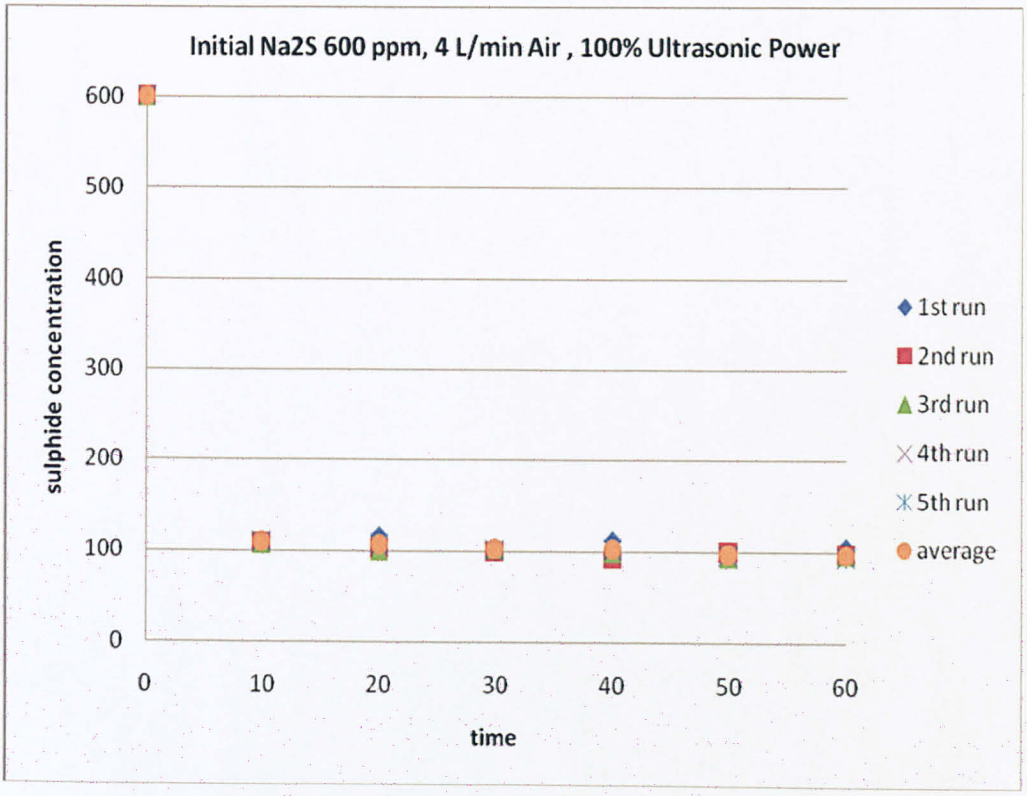
From the comparison, we can see that our method is not optimized yet. Further parameter need to be taken into account



Graph 4.2-1 Trend for 1000 ppm Initial Sulphide Content



Graph 4.2-2 Trend for 800 ppm Initial Sulphide Content



Graph 4.2-3 Trend for 600 ppm Initial Sulphide Content

4.3 Result for Different Ultrasonic Vibration Power

time	1st	2nd	3rd	4th	5th	6th	average
0	800	800	800	800	800	800	800
10	159	141.6	154.5	150.9	140.1	149.7	149.3
20	129.6	131.4	148.5	134.4	137.4	147.3	138.1
30	135.6	139.5	143.7	140.1	138.9	146.1	140.65
40	144.6	154.5	134.1	137.4	148.2	166.5	147.55
50	121.8	132.6	120.6	137.1	148.8	147	134.65
60	123.6	120.9	139.5	144.3	172.5	169.8	145.1

Table 4.3-1. 100% Ultrasonic Power ,800 ppm, 4 L/min air

time	1st	2nd	3rd	4th	5th	average
0	800	800	800	800	800	800
10	130.8	122.7	173.7	158.1	165	150.06
20	123	138	138	147	156	140.4
30	151.2	128.7	148.8	140.4	147	143.22
40	142.2	144.3	158.4	142.2	144.3	146.28
50	144	137.7	116.1	131.7	137.4	133.38
60	142.8	160.5	142.2	147.6	139.2	146.46

Table 4.3-2. 60% Ultrasonic Power ,800 ppm, 4 L/min air

time	1st	2nd	3rd	4th	5th	average
0	800	800	800	800	800	800
10	154.2	175.5	149.1	168	164	162.16
20	162.9	165	158.4	194.1	152	166.48
30	141.3	158.1	145.8	148	151	148.84
40	142.8	158.4	160.2	167.7	157	157.22
50	150.6	147.3	151.8	141	148	147.74
60	152.1	157.2	139.8	180.3	157	157.28

Table 4.3-3. 20% Ultrasonic Power ,800 ppm, 4 L/min air

100%			60%			20%		
time	DO(mg/L)	T(oC)	time	DO (mg/L)	T(oC)	time	DO (mg/L)	T (oC)
0	8.67	20	0	8.67	20	0	8.67	20
10	8.5	23.6	10	7.39	29	10	7.94	25.2
20	8.45	24.2	20	6.52	29.8	20	7.85	25.1
30	8.69	24	30	6.42	32	30	7.89	25.1
40	7.92	25.5	40	6.4	32.2	40	7.96	24.8
50	7.91	25.8	50	6.61	32	50	8.38	24.4
60	7.49	27.4	60	6.78	32	60	8.11	25

Table 4.3-4. DO and Temperature Change for Different Ultrasonic Power

time	Na_2S Average for 100% power (in ppm)	Na_2S Average for 60% power (in ppm)	Na_2S Average for 20% power (in ppm)
0	800	800	800
10	149.3	150.06	162.1
20	138.1	140.4	166.48
30	140.65	143.22	148.84
40	147.55	146.28	157.22
50	134.65	133.28	147.74
60	145.1	146.46	157.28

Table 4.3-5 Trend for Average Sulphide Drop for Different Ultrasonic Power

time	Na2S average for 100% power (ppm)	Na2S average for 60% power (ppm)	Na2S increment (ppm)
0	800	800	0
10	149.3	150.06	0.76
20	138.1	140.4	2.3
30	140.65	143.22	2.57
40	147.55	146.28	-1.27
50	134.65	133.28	-1.37
60	145.1	146.46	1.36

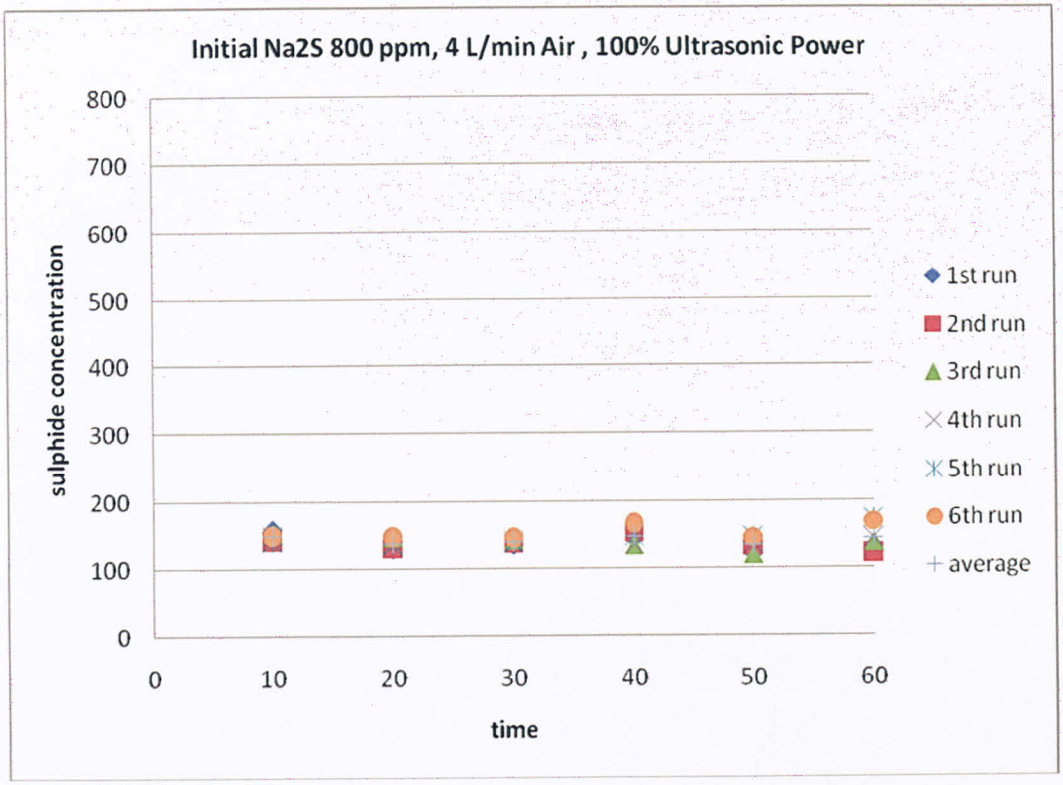
Table 4.3-6 Sulphide Increment between 100% power and 60% power

time	Na2S average for 60% power (ppm)	Na2S average for 20% power (ppm)	Na2S increment (ppm)
0	800	800	0
10	150.06	162.1	12.04
20	140.4	166.48	26.08
30	143.22	148.84	5.62
40	146.28	157.22	10.94
50	133.28	147.74	14.46
60	146.46	157.28	10.82

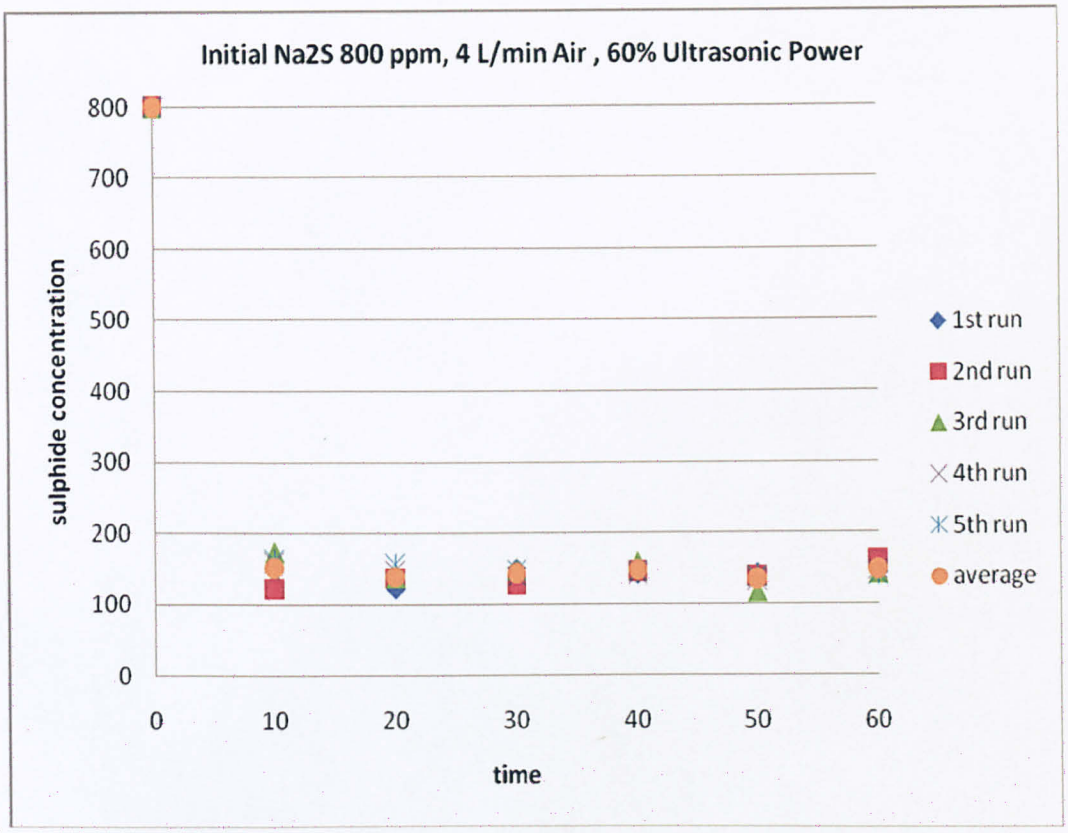
Table 4.3-7 Sulphide Increment between 60% power and 20% power

From table 4.5-2, the effect of different ultrasonic power can be seen. Interesting result can be seen here. In which the drop of Sulphide is not much between 100% power and 60%. In table 4.5-3, interesting result can be seen. The sulfide increment, when the power is reduced to 60%, is comparatively small. It is different when the power is reduced to 20%. The sulfide increment is comparatively high. The use of ultrasonic in our experiment is therefore proven success. Bachman (1937) experiment on the treatment of juices and wine using ultrasonic has shown similar effect to those resulting from a long period of aging. In the subjective opinion, the long period of aging is oxidation process. The theory from Bachman is further supported by Ensminger in 1988. Ensminger research has shown that oxidation reaction may be accelerated under the influence of ultrasonically produced cavitation *(Ensminger, 1988, pp.391).* Therefore, it is proven that the use of ultrasonic accelerated the oxidation reaction.

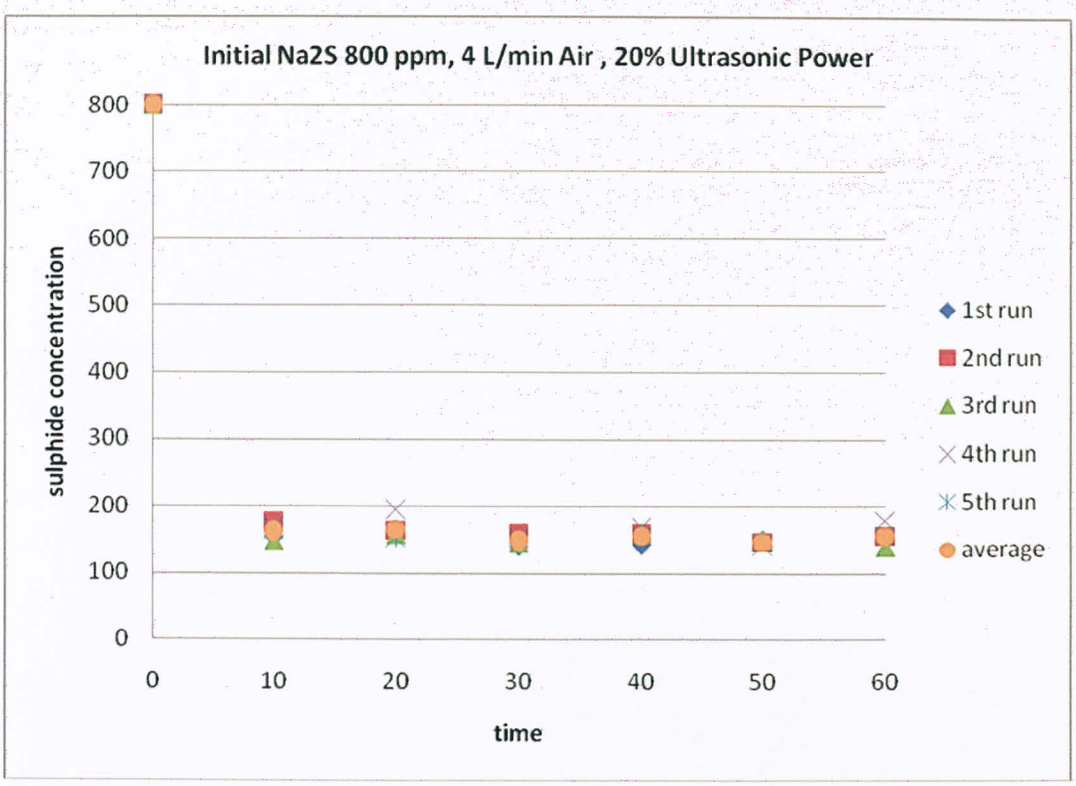
For the DO and Temperature Change, we can see that the after 60 minutes, the Sulphide which is oxidized under ultrasonic condition will face a temperature increment. The smaller temperature increment was on the 20% ultrasonic power. The temperature only rise 5 °C after 6 minutes. However, the biggest increment is on the 60% ultrasonic power. The temperature increased 12 °C from 20 °C to 32 °C.



Graph 4.3-1 Trend for 100% Ultrasonic Power



Graph 4.3-2 Trend for 60% Ultrasonic Power



Graph 4.3-3 Trend for 20% Ultrasonic Power

4.4 Result for Different Air Flow Rate

time	1st	2nd	3rd	4th	5th	average
0	800	800	800	800	800	800
10	133.2	135.3	143.4	143.1	138	138.6
20	149.4	152.7	145.5	137.1	135	143.94
30	158.1	144	155.1	168.6	154.1	155.98
40	141.3	156	157.9	166.5	143	152.94
50	141.3	140.4	158.7	156.6	139.8	147.36
60	142.2	137.4	149	147.8	140.8	143.44

Table 4.4-1. 6 L/min air, 800 ppm, 100% Ultrasonic Power

time	1st	2nd	3rd	4th	5th	6th	average
0	800	800	800	800	800	800	800
10	159	141.6	154.5	150.9	140.1	149.7	149.3
20	129.6	131.4	148.5	134.4	137.4	147.3	138.1
30	135.6	139.5	143.7	140.1	138.9	146.1	140.65
40	144.6	154.5	134.1	137.4	148.2	166.5	147.55
50	121.8	132.6	120.6	137.1	148.8	147	134.65
60	123.6	120.9	139.5	144.3	172.5	169.8	145.1

Table 4.4-2. 4 L/min air, 800 ppm, 100% Ultrasonic Power

time	1st	2nd	3rd	4th	5th	average
0	800	800	800	800	800	799.99998
10	170	161.1	156.3	173.1	167	165.5
20	163.5	180	177	190.5	178	177.8
30	149.4	147	144	170.4	149	151.96
40	139.2	135.3	180.9	171.6	145	154.4
50	137.1	138.6	152.4	147	140	143.02
60	148.5	140.4	166.5	158.7	149.3	152.68

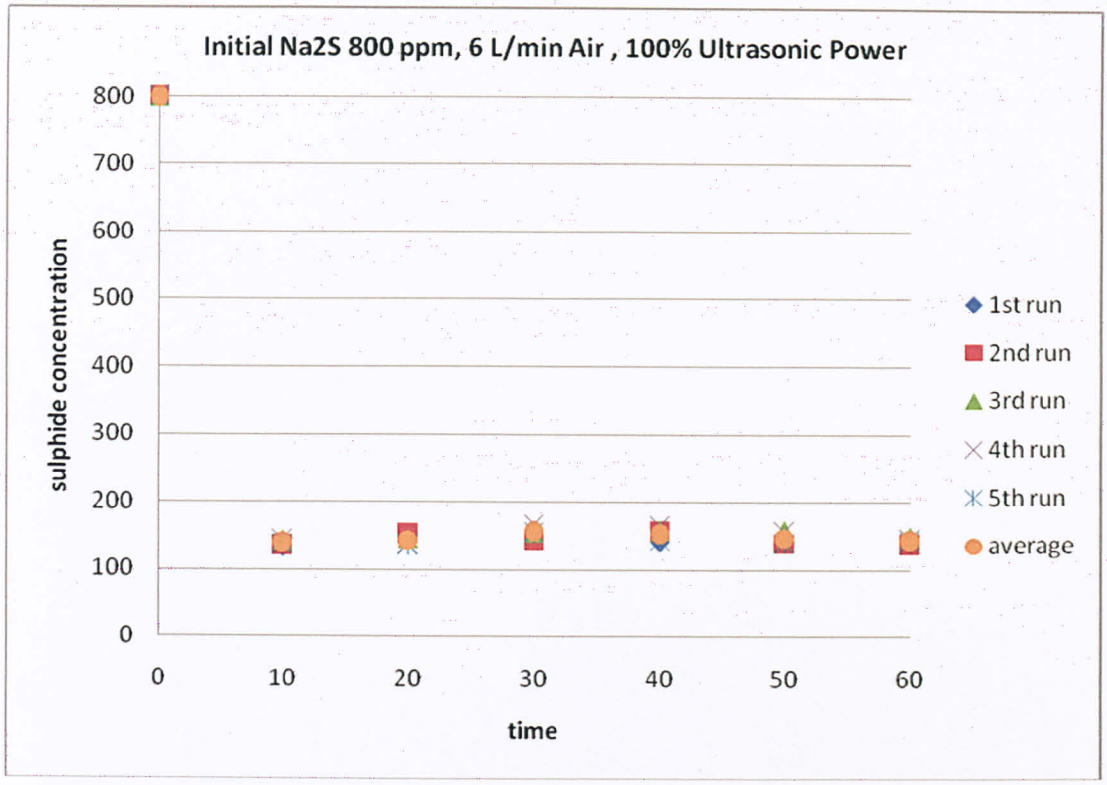
Table 4.4-3. 2 L/min air, 800 ppm, 100% Ultrasonic Power

From the table above, we can see that as the flow rate gets bigger, the Oxidation is faster. For 6 L/min, after 60 minutes time, the Sulfide drops to 143.44 L/min. For 4 L/min, after 60 minutes, the sulfide drops to 145.1 L/min. In table 4.4-1 until 4.4-3, the sudden sulfide increment can also be seen. In the column "average", the sulfide increment for 4L/min and 6 L/min happen in the 40th minutes and the 60th minutes.

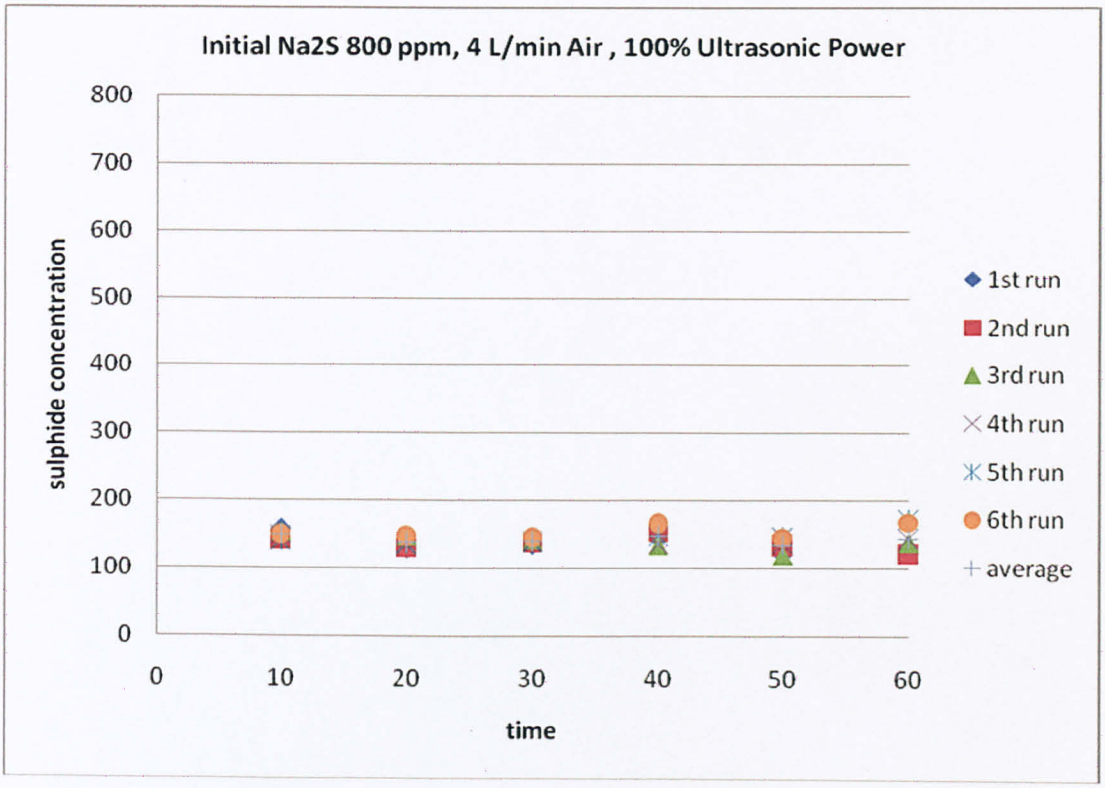
6 L/min			4 L/min			2 L/min		
time	DO (mg/L)	T (oC)	time	DO (mg/L)	T (oC)	time	DO (mg/L)	T (oC)
0	8.67	20	0	8.67	20	0	8.67	20
10	8.61	24.3	10	8.5	23.6	10	8.11	25.9
20	7.91	25	20	8.45	24.2	20	7.56	28.4
30	7.84	26.4	30	8.69	24	30	6.98	29.9
40	7.73	26.8	40	7.92	25.5	40	6.82	30.2
50	7.66	27.5	50	7.91	25.8	50	6.62	31.7
60	7.53	28.5	60	7.49	27.4	60	6.54	32.1

Table 4.4-4. DO and Temperature changes for different Air Flow Rate

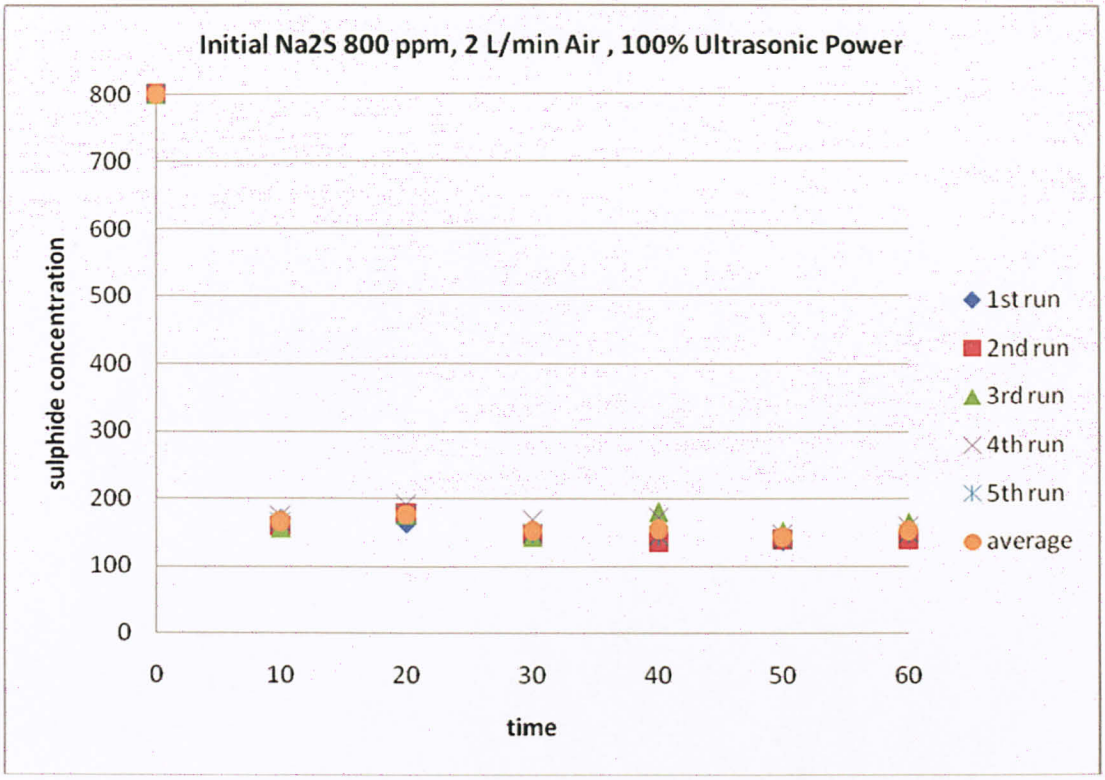
From table 4.4-4 above, the experiment result from Selmeczi still applies. The concentration of DO reduce with increase of temperature. The trend of DO is different



Graph 4.4-1. Trend for 6 L/min Air Flow Rate



Graph 4.4-2. Trend for 4 L/min Air Flow Rate



Graph 4.4-3. Trend for 2 L/min Air Flow Rate

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Technically speaking, oxidation using aeration under ultrasonic vibration is feasible to be done. The presence of ultrasonic vibrator enhances the oxidation process. However, improvement and further experiment need to be done to optimize the end product

5.2. Recommendation

Further experiment need to be done to determine:

- The model of Sulphide oxidation
- The rate of Sulphide reaction

REFERENCES

1. Alferova, LA., Titova, GA. (1969) A. Zh. Prikl. Khim 42, pp.192
2. Anon (April 11, 1983) Chem Eng News 34-35
3. Anon (January 18, 1984) Chem Weekly 29
4. Bachman, JA. (1937) US Patent 2086891
5. Bowers, JW., Fuller, MJA., Packer, JE. (1966) Chem. Ind. 8 Jan, 65
6. Chanda, M., et al (1984)Catal. 26. p. 267
7. Chen. KY., Morris, JC. (1972) Envir. Sci. Technol. 6, 529
8. Cline, JD., Richard, FA.(1969) Envir. Sci. Tech. 3. Pp.838
9. Copa, WM., Momont, JA., Beula, DA., (1992) The Application of Wet Air Oxidation to the Treatment of Spent Caustic Liquid Liquor. In Eckenfelder, Chemical Oxidation Technologies for the Nineties (pp.299-300). Pennsylvania: Weatern Hemispehere
10. Cooper, HBH., (1974) Tappi 57 pp. 130
11. Cooper, HBH., Rosano, AT (1973) Tappi 56 pp.100
12. Cooper, HBH., Rossanom, AT. AICh. E. Symp. Series No 133, Vol. 69 pp. 104
13. Couvert, A., et al. (2006) Treatment of Odorous Sulphur Compounds by Chemical Scrubbing with Hydrogen Peroxide- Application to Laboratory Plant. Chemical Engineering Science 61 (pp.7240-7248)
14. Dannenberg, S., et al. (1992) Arch. Microbiol. 158. p.93
15. Davidson, R., Palmer, WG., Forrest, TH. (1970) US Patent 3489679
16. Dietrich, MJ., Randall, TL., and Canney, PJ. (1985) Wet Air Oxidation of Hazardous Organics in Wastewater. Environmental Progress 4 no.3
17. Elvers, B., et al. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, 5th Edition, VCH, Weinheim, 1989, pp.467-485
18. Ensminger, D(1988) Ultrasonics Fundamentals, Technology, Applications. New York: Marcell Dekker Inc

19. Gourmelon, C., Boulegue, J., Michard, G. (1977) CR Acad. Scie. Paris. 284, Ser C, pp. 269
20. Kuhn et. al. (1983) J. Chem Tech Biotechnol, 33A, 406-414
21. Lempriere, BM.(2002) Ultrasound and Elastic Waves Frequently Asked Question. San Diego: Academic Press
22. Lefers, JB., Koetsier, WT., Van Swaaij, WPM. (1978) Chem Eng J 15 pp.11
23. Linkous, CA., Huang, C., and Fowler, JR. (2004) UV Photochemical Oxidation of Aqueous Sodium Sulfide to Produce Hydrogen And Sulfur. Journal of Photochemistry and Photobiology A. Chemistry 168 (pp.153-160)
24. Mallik, D and Chaudhuri, SK. (1998) Air Oxidation of Aqueous Sodium Sulfide Solutions with Coal Fly Ash. Elsevier Science Ltd (pp.585-590)
25. Mueller, JA., et al. (2002) Aeration: Principles and Practise. Vol 11.Florida: CRC Press
26. O'Brien, DJ., Birkner, FB. (1977)Envir. Sci. Technol.11, 1114
27. Sada, E., et al. (1987) Oxidation of Sodium Sulfide Solutions with Activated Carbon. Ind. Eng. Chem. Res. pp.1782-1787
28. Salazar, JR., in: RA Mayer (Ed.), Handbook of Petroleum Processes, Part 9, McGraw-Hill, New York, 1986
29. Selmeczi , JG. (1966) Preprint ACS Div. Water, Air, Waste Chem, Pittsburgh (Ch. Abs. 66, 40614)
30. Snaveley, ES. J. (1971) Petroleum Technol.April 443
31. Snavely, ES., Blount, FE. (1969) Corrosion NACE 25. pp. 397
32. Sorokin, YI. (1972) J. Cons. Int. Explor. Mer. 34,3,423 Copenhagen
33. Thomson et. al. (2008). Comparison of Methods for Processing Drinking Water Samples for the Isolation of *Mycobacterium avium* and *Mycobacterium intracellulare*. Taken from http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2394917#r13
34. www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2394917#r13
35. Ueno et. al. 1979. Water, Air, and Soil Pollution 11. Holland: D.Reidel Publishing Co.
36. Van den Bosch PLF et. al (2006) Biotechnology and Bioengineering Vol 97, No 5, August 1, 2007. Willey Intersciences
37. Wheatland, AB.(1954) Hyg Camb 52, 194

38. Mason, TJ. (1986) Ultrasonics 24(5) pp.245-253

Appendix 1.

The Wet Air Oxidation of Sulfide

at Temperature of 100 °C

Time at Temperature 100 oC (min)	Sulfide as S, mg/l
Influent	1260
15	428
30	12
45	<1
60	<1

Appendix 2.

Percent Conversion of Reduced Sulfur to Sulfate in Wet Air Oxidation